Reaction of Fused Salts with Molten Zn-Sn and Zn-Cd Alloys (1)†

Ikuo OKAMOTO*, Akira OMORI and Masaaki MIYAKE*****

Liquid amalgam have found extensive application as reducing agents in analytical chemistry[1]. The various modes of operation can be summarized by the reaction (eq. (1)).

$$O + M(Hg)_x \longrightarrow M^{n+} + R + xHg \quad (1)$$

where O is a soluble specimen in higher oxidation state, $M(Hg)_x$ is a liquid amalgam of metal M, R is the reduced form of O, and M^{n+} is the metal ion liberated from the amalgam by the reaction with O. Moreover, one can apply the reaction to prepare given amalgam $R(Hg)_{x'}$ provided O is metallic ion and R is metal of high affinity with Hg.

We use molten binary alloys (M-Sn) in place of liquid amalgam and fused metallic salts for the reaction in eq. (1), it is able to synthethize different M'-(Sn) alloy by the reaction in eq. (2), where metal M is more base than metal M'.

$$M'^{n+} + M\text{-}(Sn)\ \text{alloy} \xrightarrow{\triangle} M^{n+} + M'\text{-}(Sn) \quad (2)$$

Moreover, during soldering or brazing, where one uses a flux containing metallic salt, the variation of composition of filler metal, after bonding by the reaction of the filler metal with the metallic salt, should be taken into account.

In this report, we study the reaction of fused metallic chloride with molten binary alloys in order to know the variation of composition of filler metal after bonding, or to apply the reaction to prepare various alloys.

The reactions of various fused metallic chlorides with molten alloys were tried on Ni or Cu plate for one minute at 500°C in N_2 atmosphere. The results obtained are summarized in **Table 1** and **Table 2,** and the compositions of the alloys obtained before and after the reaction were analyzed by EPMA. The distribution of Sn, Cd and Zn, for example, is shown in **Fig. 1.** The elements are in the alloy obtained by the reaction of 10 mol% $NiCl_2$-90 mol%$SnCl_2$ salt with 84Cd-14Zn alloy on copper substrate (in Table 2). From the results in Table 1 and Table 2, it may be recognized that the reaction of metallic chloride with metal in molten alloy proceedes depending on electrochemical series[2] in pure fused chlorides in **Table 3.** For example, the reactions in eq. (3) and eq. (4) take place predominantly to give Sn-Cu alloy, since Sn and Cu are more noble than Zn, when 20 mol%-$CuCl_2$-80 mol%$SnCl_2$ salt and 84Sn-16Zn alloy are used.

Table 1. Composition of alloys obtained by dissolution of Cu from $CuCl_2$ flux in various alloys measured by EPMA.

Flux	Alloy (w/o)	Approximate composition of alloy after reaction by EPMA (w/o)				
		Cu	Sn	Ni**	Zn Zn	Cd
20 mol% $CuCl_2$-$SnCl_2$	Sn	10	86	4	—	—
	84Sn-16Zn	11	86	3	no detect	—
	86Cd-14Zn	5	87	1	no detect	7
20 wt% $CuCl_2$-KCl/LiCl*	Sn	17	81	2	—	—
	84Sn-16Zn	17	82	1	no detect	—
	86Cd-14Zn	13	—	6	5	76

* eutectic salt
** from base plate

† Received on July 22, 1974
* Professor
** Research Instructor
*** Co-operative Researcher (1974), Assistant Professor, Junior College of Engineering, University of Osaka Prefecture

Table 2. Compositions of alloys obtained by dissolution of Ni from $NiCl_2$ flux in various alloys measured by EPMA.

Flux	Alloy	Ni	Sn	Cu**	Zn	Cd
10 mol% $NiCl_2$-$SnCl_2$	Sn	3	83	14	—	—
	84Sn-16Zn	4	83	13	no detect	—
	86CD-14Zn	3	78	10	2	7
20 wt% $NiCl_2$-KCl/LiCl*	Sn	11	65	24	—	—
	84Sn-16Zn	16	79	5	no detect	—
	86Cd-14Zn	8	—	7	5	80

* eutectic salt
** from base plate

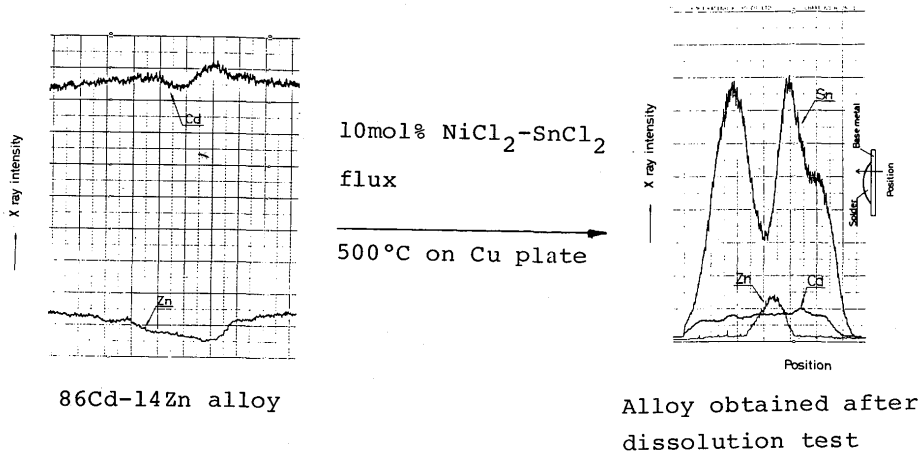

Fig. 1. Distribution of Sn, Zn and Cd in alloy obtained before and after dissolution test of Ni from 10 mol% $NiCl_2$-$SnCl_2$ system flux in 84Cd-14Zn alloy on Cu plate.

Table 3. Electrode potentials of metals in pure fused chloride at 700°C. $E_{Na}=0$.

Electrode	Volt
K/K^+	-0.14
Li/Li^+	-0.02
Zn/Zn^{2+}	+1.96
Cd/Cd^{2+}	+2.11
Sn/Sn^{2+}	+2.31
Ni/Ni^{2+}	+2.36
Cu/Cu^+	+2.65

$$SnCl_2 + Zn\text{-}(Sn) \longrightarrow ZnCl_2 + Sn\text{-}(Sn) \quad (3)$$

$$CuCl_2 + Zn\text{-}(Sn) \longrightarrow ZnCl_2 + Cu\text{-}(Sn) \quad (4)$$

Also, the reactions in Table 1 and Table 2 may proceed on the basis of electrochemical series of metal (Li, K, Zn, Cd, Sn, Ni, Cu). However the reactions may be barely influenced eigher by the dissolution of metal of base plate, or by the easinesss of the dissolving of metal from chlorides, or by solvent effect. Further detailed investigations are expected in near future.

References

1) W. G. Scribner and C. N. Reilley: Indirect Complexometric analysis with Aid of Liquid Amalgams, Anal. Chem. Vol. 30, (1958) No. 9, 1452.

2) O. Kubashewski, E. L. I. Evans and C. B. Alcock: Metallugical Thermochemistry 4th edition, Pergamon Press Limited, England (1967) p. 354.